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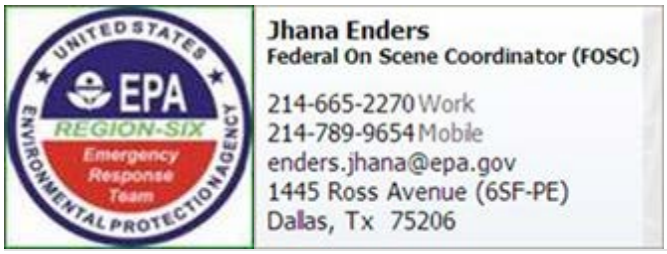
| **From:** | Turner, Philip |
| **To:** | Enders, Jhana |
| **Subject:** | RE: Laboratory Questions and response |
| **Date:** | Thursday, March 2, 2017 1:47:00 PM |
| **Attachments:** | image004.png |

Hmmm… I'm thinking lab-spiked samples first

**From:** Enders, Jhana
**Sent:** Thursday, March 02, 2017 1:22 PM
**To:** Turner, Philip
**Subject:** RE: Laboratory Questions and response
Trial run with field samples or other?




**From:** Turner, Philip
**Sent:** Thursday, March 02, 2017 1:17 PM
**To:** Enders, Jhana <Enders.Jhana@epa.gov>; Smith, Terry <Smith.Terry@epa.gov>
**Subject:** RE: Laboratory Questions and response
Again, this is why it would be nice to have a lab do some sort of trial run…

**From:** Enders, Jhana
**Sent:** Thursday, March 02, 2017 12:42 PM
**To:** Smith, Terry <Smith.Terry@epa.gov>
**Cc:** Turner, Philip <Turner.Philip@epa.gov>
**Subject:** Re: Laboratory Questions and response
With all that said, is there any way to use existing data w additional lab input to have more confidence in the data already received? With no guarantee the NIOSH will be any better, just need a good call on whether it is worth resampling...

Sent from my iPhone

On Mar 2, 2017, at 12:24 PM, Smith, Terry <Smith.Terry@epa.gov> wrote:

> Jhana and Phil: My comments.
> Terry
> 1) What is the lab's 'historical experience?" Have they done one, twenty, hundreds?...additional info needed to evaluate this response better.
> ***Our QA manager reviews the data trends for each method annually based on QC recoveries. The current limits are based on our historical QC data trends since 2015 to present which in compasses 15 batches or 200 samples. Attached a summary provided by our QA manager showing the calculated uncertainty for the OSHA 1003 method performed by our laboratory.***
> TSmith Response: The lab does have some experience in analyzing phosphine using the

OSHA method. The issue here is that I would expect most, if not all, of these analysis are performed for worker protection, and are therefore analyzed at the much higher concentrations needed for workers than what the need for Region 6 is (i.e. 0.31 ug/m3). Therefore historical QC limits and method performance provided by the lab probably does not correlate with what might be expected at the 0.3 ug/m3 limits.

2) Please explain a bit more about the process of 'field blank correct the samples.'

***If a client submits a field blank which contain measurable contamination for the analyte of interest. The case can be made that the active field samples can be subtracted by the amount found in the field blank to correct for any interferences or media back ground contamination. Our laboratory runs a Laboratory Media Blank (LMB) standard along with spiked quality control samples from the same lot. Our practice to correct for media background contamination is to subtract the amount of the contaminant found in our LMB from our internal Quality control spiked media. However, it is not our laboratories standard practice to make the same correction to the client's field samples. Two reason for this practice:***

a) ***Laboratory cannot guarantee that the client submitted media from the same lot used by the laboratories QC spikes.***

b) ***We prefer that the client have control on how to interpret their data based on how their field quality control sample perform***

TSmith Response: It is not an EPA practice to subtract field blank or media (lot) blank results from field sample results. Overall site decision making is performed taking into consideration results from field samples, as well as field blanks, trip blanks, etc., but blank subtractions are not performed. The ALS lab mentions their practice of correcting for media background contamination. However, this appears to only be performed on the internal QA spiked samples (e.g. MS/MSD). They are not saying they correct field sample results using the media blank results.

**Sent:** Wednesday, February 22, 2017 8:21 AM

Below are the laboratory's response (**bold blue**) to the questions from yesterday's conference call:

1) Our client is concerned that the method detection limit of 13 µg/m$^3$ listed on page 4 of 15 under section 1.2.2 was not achieved. Would it be possible for you to report the results to include your Method Detection Limit (MDL) not just the Report Limit (RL)?

   a. ***Unfortunately, we do not have the option to report lower than our current Reporting Limit for OSHA 1003 method. The current reporting limit has been established based on historical experience with this method and media background interferences.***

TSmith Response: Most NIOSH and OSHA air methods do not include Method Detection Limits as per many of the EPA Methods. MDL, as defined in EPA terminology, is a statistical evaluation of replicate analysis of samples spiked at concentrations estimated to be a factor of 3 or 4 times an estimated MDL. These requirements are not written In OSHA or NIOSH methods, and are therefore not performed by the labs. A determination of an MDL, using EPA protocols, is probably not appropriate for required reporting limits of 0.3 ug/m3 anyway. A

more realistic approach would be to have the lab prepare in-house standard at the 0.3 ug/m3 level to determine if they actually can detect at that level.

2) Please provide a detailed explanation of why phosphorus was detected above the RL in the Laboratory Media Blank (LMB) at 6.15 µg/sample? The phosphorous concentration present in the LMB is very similar to detections in the samples thus making the validity of the data questionable.

    a. ***On occasion, we do see background contamination on the media which can vary from lot to lot. I believe we sent the media for the project and also used the same media lot for the quality control. Assuming your sample PH3-FB-28012017-85 filter came from the same lot as the one used by our laboratory, the levels found are in line with our laboratory LMB result. If needed, we can field blank correct the samples.***

TSmith Response: I am not sure of the historical values for the media from lot to lot. The needed approach would be for the lab to analyze a subset of the media lot that will be sent to the field for sample collection before sending to the field. If the lot sample is contaminated, then a new lot should be tested. If continuous lot subsamples give consistent contamination levels at the 0.3 ug level, then that type of media probably should not be used.

3) If the site was re-sampled what are the chances that the Laboratory Reagent Blank (LRB) and/or LMB would again show phosphorus contamination?

    a. ***The reagent blank was non-detect down to our reporting limit. I would not expect this outcome to be any different on the next round of samples. However, depending on the lot used for the treated media (LMB and QC), there exist the possibility that there may be some inherent contamination from lot to lot.***

TSmith Response: See response above. Need to analyze a subset of the lot before using the media in the field.

4) Would it be possible to lower the MDL and/or RL by increasing the sample volume above the 240L and/or training filters?

    a. ***The only variable available to adjust is the collection volume. The OSHA 1003 method recommends a maximum collection volume of 240 L. Based on the recipe provide within the method, I calculated a theoretical maximum loading of 4 mg/sample of phosphine that can be collected on the treated media. Meaning, based on the levels reported, there appears to be room to extend the collection volume beyond the 240 L recommended maximum. I would strongly recommend someone double check my calculation based on the follow parameters:***

TSmith Response: The approach presented by ALS is theoretical. The best approach is to test in the lab first by spiking a media, and then pulling the required volume of air through the media, and then analyzing the sample in the lab to ensure there is no breakthrough. For the NIOSH method it is common to place two media tubes in series. The lab will run both tubes to see if the second tube contains the analyte, indicating there was breakthrough of the first tube.

**in 40.0 mL of 95:5 (v/v) methanol/glycerol was prepared. Caution: Mercuric chloride is a poison and slightly volatile at ordinary temperature. Forty cleaned filters were placed on a clean glass plate and, using an Eppendorf pipet with a plastic tip, 0.95 mL of the mercuric chloride solution was applied to each filter. $PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$**

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**From:** Enders, Jhana
**Sent:** Thursday, March 02, 2017 11:35 AM
**To:** Smith, Terry <Smith.Terry@epa.gov>
**Subject:** Laboratory Questions and response

Terry,

See the comments START received from the lab below and let me know your thoughts…The meeting with UC is 3:30 today (CST). Thanks.

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**A solution of 4.0 g of mercuric chloride and a small amount of methyl orange in 40.0 mL of 95:5 (v/v) methanol/glycerol was prepared. Caution: Mercuric chloride is a poison and slightly volatile at ordinary temperature. Forty cleaned filters were placed on a clean glass plate and, using an Eppendorf pipet with a plastic tip, 0.95 mL of the mercuric chloride solution was applied to each filter.** $PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$